TITLE: Variable, Kinetics and Mechanisms of Heterogeneous Reburning

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ABSTRACT

OBJECTIVES

The objectives of this project were

1. to quantify the extent of heterogeneous mechanisms during reburning involving chars derived from coals and lignites,
2. to evaluate the process potential of heterogeneous reburning by investigating its variables and kinetics, and,
3. to examine the possible mechanistic implications derived from the parameter and kinetic studies.

ACCOMPLISHMENTS

Simulated reburning were conducted with a bench-scale flow reactor equipped with gaseous, liquid and solid fuel injection ports, and analyzers for product analyses. NO reduction rates were estimated by taking into account the experimentally observed NO conversion in the heating-up, isothermal and cooling zones of the reactor, laminar flow profile, and mass transfer limitations.

It was demonstrated in the early phase of the project that the extent of heterogeneous reactions on the lignite char surface contribute a high level of NO reduction in reburning environments, which is comparable to that in the gaseous phase during lignite reburing. The comparison was based on approximately the same amount of carbon in each phase.

In the parameter study, the efficiency of heterogeneous reburning was found to depend on the origin of the char, char preparation history, and the presence of oxidants, CO_2 and O_2, and the reducing agent, CO, in reburning. In the absence of CO_2 and O_2, the intrinsic rate of NO reduction by a lignite char, based on per unit surface area, is comparable to that of a bituminous-coal char. The intrinsic rate constants of surface NO reduction in various gaseous environments have been estimated and compared with those published.

In addition to its large surface area, the effectiveness of lignite char appears to be attributable to its ability to promote two consecutive reactions: 1) the gasification of char by CO_2 and O_2 for production of CO, and, 2) the removal of surface oxygen complexes, including those formed after adsorption of NO, by gaseous CO, for the regeneration of reactive sites, C_f, i.e.,

$C(O) + CO \rightarrow C_f + CO_2$

Lignite chars, particularly those from less severe pyrolysis, reacts vigorously with CO_2 and O_2 during reburning, and produce CO at a concentration as high as 1%. Carbon monoxide effectively scavenges the oxygen complexes on the char surface and liberates the reactive sites, thus, resulting in sustained shuttling of oxygen atoms and substantial reduction of NO. This role of CO is supported by the following observations.

1. Within the experimental ranges of the current study, high NO reduction is always accompanied with high CO production in the isolated reburning stage.
2. Introducing additional CO in the feed of the simulated reburning with lignite char promotes further NO reduction; the additional NO reduction is accompanied with noticeable CO_2 production.
3. Effective NO reduction has been observed when a mixed fuel, containing methane and lignite ash or char, is used for reburning.
4. The intrinsic rates of NO reduction estimated by resorting to the conversion in a flow reactor are usually higher than those from differential, fixed bed reactors, signifying the possible role of secondary reactions between the volatile products and the entrained char, such as scavenging of surface oxygen complexes by CO.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The role of CO in scavenging surface oxides may play an important, if not principal, role in a number of well documented combustion phenomena involving low NO productions. For instance, the commonly observed low conversions of lignite nitrogen in primary flames in comparison with that of a bituminous coal is likely due to the rapid, catalytic production of CO followed by CO scavenging of surface oxides during lignite combustion. It is also known that the flue gas of fluidized-bed combustion of lignite has lower NO concentrations than those from the pulverized coal combustion, and the interactions among NO, CO and lignite char in the dense phase of the bed may have contributed to the low-NO productions in the former.

The role of CO discussed above implies that the use of a mixed fuel, containing a volatile fuel for CO production and lignite char for catalytic NO reduction, can be a potentially very attractive technology for NO reduction. The use of a mixed fuel minimizes the requirement of feeding a large amount of solid reburning fuel. For maximum NO reduction, separate feeding of volatile and solid fuels also allows more feeding options, such as feeding sequence and geometry. Moreover, we have observed that lignite char or ash catalyzes the conversion of HCN to NH_3; HCN is a major intermediate which has a higher recycle ratio to NO than NH_3 in the burnout stage. These characteristics of lignite char render the possibility of operating the advanced reburning at stoichiometric ratios much higher than those normally used, SR2 = 0.8 to 0.9, for effective NO reduction, and, therefore warrants minimum production of CO and unburned hydrocarbons in the burnout stage.

The chars adopted in this project were derived from pyrolysis and no attempts have been made to chemically or physically activate the chars. Since the pyrolysis chars have surface areas only about 10% of the activated carbons in the market, it is anticipated that the reactivities of chars can be enhanced dramatically after proper activation. Alternatively, this study also implies that lignite char may be a potentially valuable raw material for the production of catalysts for NO reduction.

LIST OF PUBLICATIONS, PRESENTATIONS AND STUDENTS SUPPORTED UNDER THIS GRANT

Refereed Journal Articles

Chen, W.Y., and L. Ma, "*Effects of Heterogeneous Mechanisms during Reburning of Nitrogen Oxide*," AIChE Journal, **42**(7), 1968-1976 (1996).

Chen, W.Y., "*Rate Measurement with a Laboratory-Scale Tubular Reactor*," Chemical Engineering Education, **33**(3), 238-243 (1999).

Tang L. and W.Y. Chen, "Improvements on a Particle Feeder for Experiments Requiring Low Feed Rates," Review of Scientific Instruments, **70**, 3143-3144 (1999).

Chen, W.Y., and L. Tang, "*Variables, Kinetics and Mechanisms of Heterogeneous Reburning*," Under minor revision for the AIChE Journal (2001).

Partial List of Conferences Papers

Chen, W.Y., "*Formation and Destruction of Nitrogen Oxides during Coal Combustion*," Proceedings of the Second Mainland-Taiwan Environmental Protection Seminar, Vol. 2, pp. 597-605, Taipei, Taiwan, December 21-26, 1993.

Burch, T.E., and W.Y. Chen, "*Tracing of NO Formation and Destruction in Reburning by Isotope-Labeling Technique*," Presented at the Annual AIChE Meeting, Paper #77r, San Francisco, California, November 13-18, 1994.

Chen, W.Y., and L. Ma, "*Importance of Heterogeneous Mechanisms during Reburning of Nitrogen Oxide*," Proceedings of the Third International Symposium on Coal Combustion, Beijing, China, pp.594-601, September 18-21, 1995.

Chen, W.Y., and L. Ma, "*Char-Enhanced Reburning of Nitrogen Oxide*," Presented at the Annual meeting of the American Institute of Chemical Engineers, Paper #78k, Miami Beach, Florida, November 12-17, 1995.

Chen, W.Y., "*Heterogeneous Reburning of Nitrogen Oxide*," Proceedings of the 1996 Chinese American Academic and Professional Convention, pp.4.19.1- 4.19.4, Ottawa, Canada, June, 29 - July 2, 1996.

Chen, W.Y., "*Effects of Oxidants on NO Reduction on Chars of Different Origins*," presented at the Annual Meeting of the American Institute of Chemical Engineers, Paper#122v, Chicago, Illinois, November 10-15, 1996.

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Chen, W.Y., and L. Tang, "*Parameters, Kinetics and Mechanisms of Heterogeneous Reburning*," Proceedings of the 23rd Biennial Conference on Carbon, pp.384-385, State College, Penn., July 13-18, 1997.

Chen, W.Y., and L. Tang, "*Variables, Kinetics and Mechanisms of Heterogeneous Reburning*," presented at the Annual Meeting of the American Institute of Chemical Engineers, #185i, Los Angeles, CA, November, 16-21, 1997.

Chen, W.Y., and L. Tang, "*Further Investigation of Heterogeneous Reburning*," presented at the 5th Mainland-Taiwan Environmental Protection Seminar, Nanjing, China, May, 26-30, 1998.

Chen, W.Y., "*Simplified Tubular Reactor Models for Rate Measurement*," presented at the Annual Meeting of the American Institute of Chemical Engineers, #318at, Miami Beach, FL, November 15-20, 1998.

Tang, L., and W.Y. Chen, "*Improvements on A Particle Feeder for Bench-Scale Experiments Requiring Low Feed Rate*," presented at the Annual Meeting of the American Institute of Chemical Engineers, #318ap, Miami Beach, FL, November 15-20, 1998.

Chen, W.Y., "*Parameters, Kinetics and Mechanisms of Heterogeneous Reburning*," presented at the Second Annual Memphis Area Engineering Societies Conference, May, 11, 2000.

Chen, W.Y., "*Role of Carbon Monoxide during Heterogeneous Reburning of Nitrogen Oxide*," presented at the Annual Meeting of the American Institute of Chemical Engineers, Paper #39g, Los Angeles, California, November 12-17, 2000; Proceedings of the Topical Conference on Energy and the Environment, pp.128-131.

Invited Seminars

Chen, W.Y., *"Formation and Destruction of Nitrogen Oxide during Coal Combustion,"* Tunghai University, Taichung, Taiwan, December 28, 1993.

Chen, W.Y., *"Stochastic Modeling," "Emissions of Nitrogen Oxide during Coal Combustion,"* and "*Particle Size Distribution after Primary Fragmentation of Coal: an Application of the Maximum Entropy Formalism*," National Cheng-Kung University, Tainan, Taiwan, December 29, 1993.

Chen, W.Y., *"Emissions of Nitrogen Oxide during Coal Combustion,"* Industrial Technology Research Institute, Hsinchu, Taiwan, December 30, 1993.

Chen, W.Y., *"Nitrogen Reaction Chemistry during Coal Combustion,"* Christian Brother University, March 31, 1994.

Chen, W.Y., *"Air Pollution - Sources, Effects and Control,"* University of Mississippi, September 1, 1994.

Chen, W.Y., "*Role of Char during Reburning of Nitrogen Oxide*," Prairie View University, August 10, 1995.

Chen, W.Y., "*Mechanisms of Nitrogen Oxide Formation and Destruction*," Tsinghua University, Beijing, China, September 22, 1995.

Chen, W.Y., "*Mechanisms of Nitrogen Oxide Formation and Destruction*," Xian Jiaotong University, Xian, China, September 25, 1995.

Chen, W.Y., "*Heterogeneous Reburning for the Control of Nitrogen Oxide During Stationary Combustion*," The City College of the City University of New York, May 11, 1998.

Chen, W.Y., "*Heterogeneous Reburning for the Control of Nitrogen Oxide During Stationary Combustion*," The University of Arkansas, Fayetteville, Arkansas, March 11, 1999.

Chen, W.Y., "*Heterogeneous Reburning for the Control of Nitrogen Oxide During Stationary Combustion*," Tunghai University, Taichung, Taiwan, May 22, 2000.

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